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Effect of boron promotion on the performance of Pt/Al_2O_3 catalysts during propane dehydrogenation

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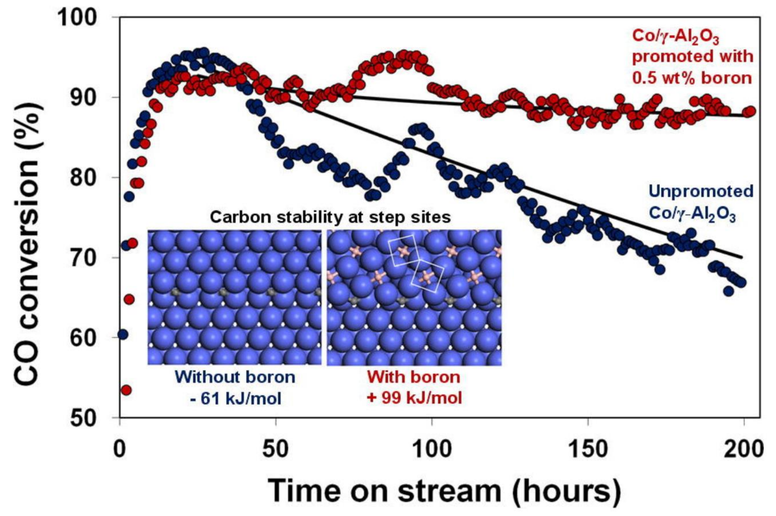
Introduction

Bimetallic Pt catalysts such as PtSn, PtGa, PtIn and PtGe, have received considerable attention to enhance the yield and stability in dehydrogenation reactions. The addition of promotors enhances the catalyst lifetime by reducing carbon deposition (coking) and/or sintering.

Motivation

Boron promotion enhances the stability of Ni and Co catalysts without affecting their activity and selectivity in steam reforming and Fischer-Tropsch synthesis, and improves selectivity of Pd catalysts in hydrogenation reactions. In this work we evaluate whether this concept extends to Pt catalysts.

Refs: Saeys, et al., J. Catal. **2009**, J. Catal. **2011**

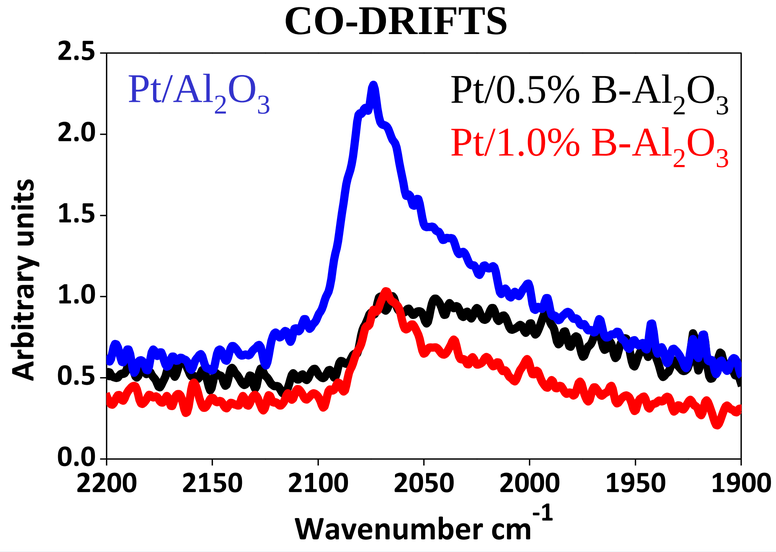


Characterization

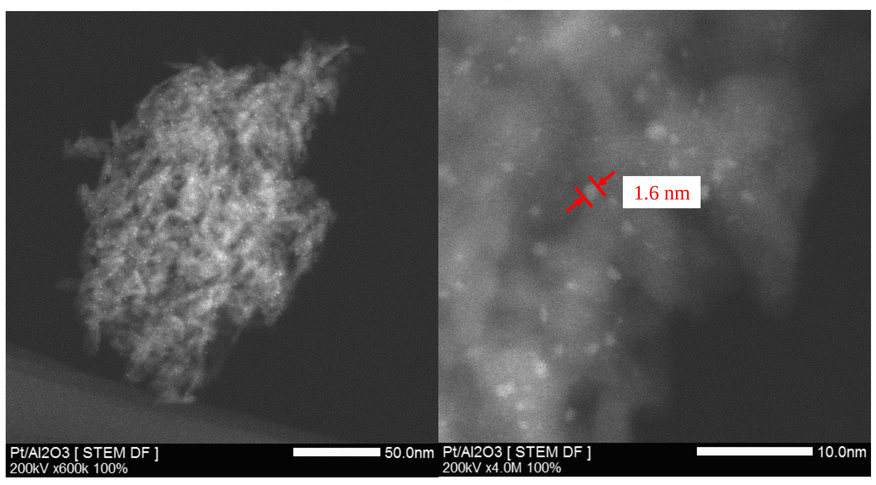
Catalyst	D (%)
3% Pt/Al_2O_3	23
3% Pt/0.5% B-Al_2O_3	17
3% Pt/1.0% B-Al_2O_3	4

B promoted Pt/Al_2O_3 catalysts were prepared with 3 wt.% Pt and B loadings up to 1.5 wt.%.

CO-DRIFTS



TEM Images

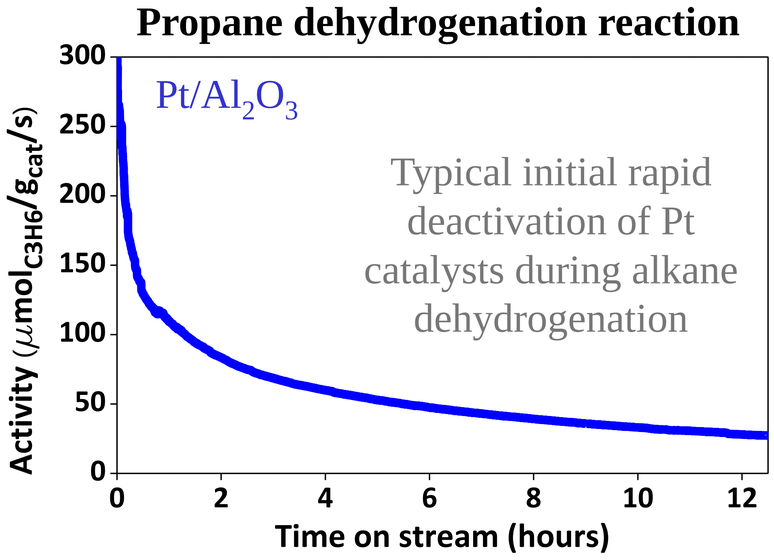


Activity and Stability

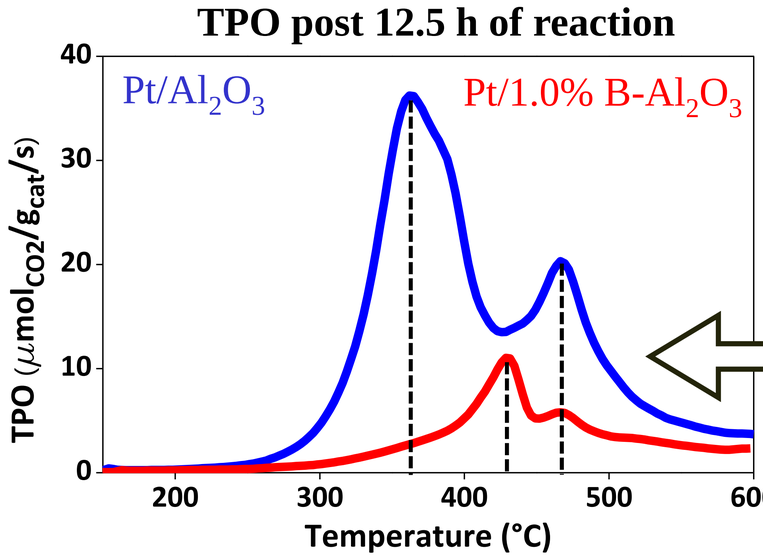
Catalyst	Activity (µmol $C_3H_6/g_{cat}/s$)	S_{C3H6} (%)	Activity Decay (%)	TPO post reaction (µmol $CO_2/g_{cat}/s$)
Pt/Al_2O_3	27	98	91	1500
Pt/1.0% B-Al_2O_3	23	98	83	**340**

Conditions: 600 °C, 1 bar, C_3H_8/H_2/He:1/1/3. Results after 12.5 h

Propane dehydrogenation reaction



TPO post 12.5 h of reaction



Support	TPO post polymerization (µmol $CO_2/g_{cat}/s$)
Al_2O_3	290
1.0% B-Al_2O_3	11

Propylene polymerization at 600 °C, 1 bar, C_3H_6/He:1/9 for 30 min.

- ✓ **Two types of coke are present on the catalyst surface.**
- ✓ **Strong effect of B on the coke formed on Pt (first peak).**
- ✓ **B promotion also reduces coke formation by polymerization on support acid sites (second peak).**

Computational catalysis

B position	Binding energy (kJ/mol)
Fcc	-626
Subsurface	-641

Boron binds strongly at subsurface octahedral sites. B removal by hydrogen is highly unfavorable (ΔG_{rxn} = + 157 kJ/mol).

Conclusion

The addition of small amounts of boron improves the stability and reduces the amount of coke formation on Pt/Al_2O_3 catalysts during propane dehydrogenation. It affects both the metal sites and the support acid sites.

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This work was supported by an Odysseus grant from the Research Foundation-Flanders. Financial support of CONICET for scientific visit of postdoctoral fellows is gratefully acknowledged.